Nanoconfined Polystyrene: A New Phase

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Abstract

Transverse layering of molecular gyration spheres in spin-coated atactic polystyrene (aPS) films, for film thickness $R \leq 4R_g$ (R_g = unperturbed gyration radius), causes an increase in free energy that does not follow the $(R_g/R)^{-2}$ dependence of planar confinement and is explained by invoking a fixed-range, repulsive, modified Pöschl-Teller intermolecular potential, its strength decreasing with increase in R. Vacuum ultraviolet spectroscopy reveals a change in 'physical dimers' of adjacent pendant benzene rings of aPS from 'oblique' to 'head-to-tail' configuration as film thickness goes from $9R_g$ to $2R_g$. This reduces cohesion by reducing dimer dipole moment. Thus a new phase of aPS, the nanoconfined phase, ordered but with lower cohesion than bulk, is formed.

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One-dimensional geometrical confinement of fluids causes the fluid to form layers normal to the confinement direction [1, 2, 3]. For such 'nanoconfined' simple fluids the layer periodicity is equal to the molecular size while for polymers (complex fluids) it is equal to the unperturbed gyration radius (R_g) [2], i.e., the dimension of a polymer molecule in the maximum entropy configuration [4]. Nanoconfined fluids exhibit radically new mechanical, thermal, dielectric and rheological properties [5, 6] . In a very recent study, a nanoconfined simple liquid has been observed to be in a 'laterally cooperative' state that behaves liquid-like or solid-like depending on the kinematics of the measurement process [7]. In polymers layers form only when film thickness is less than $4R_g$ and there is a reduction in cohesion between adjacent molecular gyration spheres [8], i.e. an increase in free energy. These new properties suggest a basic reorganization at molecular levels and they are bound to have strong implications in any technology employing thin fluid films such as optoelectronic and magnetic coatings, adhesives, biological membranes and emerging nanotechnologies, in particular, photonics and nanofluidics.

In this communication we show that the increase in free energy due to layering does not tally with that observed for planar confinement [9, 10]. We find, from tapping-mode atomic force microscopy studies, a very similar confinement-induced reduction in cohesion between adjacent gyration spheres on the film surface. We have explained this drop in cohesive interaction as the emergence of a new, repulsive intermolecular potential that fits well with a modified Pöschl-Teller potential(MPT) [11], whose depth can be increased by thinning the film but whose range is invariant with confinement. We have also shown, through vacuum ultraviolet (vuv) spectroscopy, that confinement causes a change in the geometry of pairs ('physical dimers') of adjacent pendant benzene rings in polystyrene from 'oblique' to 'head-to-tail' that reduces the dipole moment of each 'dimer', which in turn, reduces cohesion between molecular gyration spheres.

Atactic polystyrene (aPS, mol. wt. $M \simeq 560900$, $R_g = 0.272M^{\frac{1}{2}} \simeq 20.4$ nm) [12] was spin-coated on fused quartz plates from toluene solutions using a photo resist spin-coater (Headway Inc.) to form films with thickness (R) varying from 40 nm ($\simeq 2R_g$) to 180 nm ($\simeq 9R_g$), and with air/film and film/substrate interfacial roughness ~ 0.6 nm, as has been described previously [8]. Contaminants are removed from the substrate by boiling it with 5:1:1 H_2O : H_2O_2 : NH_4OH solution for 10 minutes, followed by rinsing in acetone and ethyl alcohol.

Atomic Force Microscopy (AFM) images were acquired in tapping-mode with Nanoscope IV, Veeco Instruments, using etched Si tip and Phosphorus doped Si cantilevers. The free amplitude was $\mathsf{A}_0 = 36$ nm, set point amplitude $\mathsf{A} = 10.94$ nm, cantilever quality factor $Q = 505$, resonance frequency $\omega_0 = 2\pi$ 283 kHz and spring constant $k = 20$ Nm^{-1}. x-ray reflectivity (XR) data of polystyrene films were collected using the Cu $K_{\alpha 1}$ line ($\lambda =$ 0.1540562 nm) from an 18 kW rotating anode x-ray generator (Enraf Nonius FR591), and Electron Density Profiles (EDPs) along film thickness were obtained using standard methods of analysis [2, 8].

Figure 1(a) shows the reflectivity profiles (open circles) of aPS films of different R-values, and the extracted EDPs from best fits (line) are shown in Figure 1(b) in the same sequence and having the same color code. For $R \leq 4R_g$ (84.0 nm) we observe formation of layers in aPS parallel to the substrate surface, the error in ρ being an order of magnitude less than this variation [2]. The reduction in cohesive energy caused by the variation of density due to layering is given by [8, 12, 13]

$$\begin{aligned} \Delta G^{(o)}_{PS-PS} &= -\Delta A^{(o)}_{PS}/(2.1 \times 10^{-21}) \\ &= -\sigma_{PS}(\rho(z)^2 - \rho^2_{max})/(2.1 \times 10^{-21}) \end{aligned} \tag{1}$$

where $\Delta G^{(o)}_{PS-PS}$ is the reduction in (out-of-plane) cohesive energy caused by the variation of density due to layering, $\Delta A^{(o)}_{PS}$ is the (out-of-plane) change in polystyrene Hamaker constant, σ_{PS} is the polarizability of aPS and $\rho(z)$ (ρ_{max}) denotes the electron density at depth z (corresponding maximum).

Figure 1(c) shows the variation of $\Delta A^{(o)}_{PS}$ with (R_g/R), obtained from Eqn (1). The continuous line is the best fit to the data (open circles) with the function

$$\Delta A^{(o)}_{PS} = K(R_g/R)^b \tag{2}$$

The value of b obtained from this fit is 3.0 ± 0.3. This deviates clearly from $b = 2$, for an ideal polymer, or from $b = 1.7$, for a self-avoiding polymer [9], under planar confinement [10] and, rather, correspond to spherical confinement [9] of the polymer. We are thus led to study the variation of surface free energy of the polymer films with R to inspect for any deviations from planar confinement.

Figures 2(a) and 2(b) show the phase images obtained from tapping-mode AFM of two typical aPS films with $R \simeq 50.0$ nm and 84.0 nm, respectively. The topographical images

of all these films show roughly spherical features with an average diameter of R_g [8], corresponding to gyration spheres. The frusta ($\simeq$ 0.6 nm high) of these spheres are consistent with the top roughness obtained from x-ray studies. But the phase images show larger variations in phase-shifts between adjacent 'spheres' on film surface as R reduces from 84.0 nm to 40.0 nm, implying a larger variation in energy dissipated by the AFM tip in going over from sphere to sphere [14] and, by extension, a spatial variation in surface free energy that increases with decrease in R. This spatial variation is not observed for $R > 4R_g$ and it cannot be explained by simple planar confinement of the polymer. Thus, above a certain degree of confinement, the very nature of confinement is changed by the formation of layers. We have tried to find out what exactly is changing in the films from the layering induced variations in free energy along film-depth, presented above, and on film-surface, discussed below.

To the end of determining the variation in surface free energy caused by layering, we have estimated the average energy dissipated per cycle by the tip over the film surfaces, E_D, using the expression [14]

$$\sin\phi = \left(\frac{\omega}{\omega_0}\frac{\mathsf{A}}{\mathsf{A}_0}\right) + \frac{QE_D}{\pi k \mathsf{A}\mathsf{A}_0} \tag{3}$$

where ϕ is the phase-shift with respect to the drive signal and the other terms have been described above.

The tip exerts a van der Waals force on the surface, during approach and retraction. This interaction is modeled as a sphere approaching a plane with an effective contact area $4\pi r_c \alpha_{Si}$, where r_c is radius of tip-curvature ($\simeq$ 10nm) and α_{Si} is the Si atomic diameter (= 0.22nm). Then energy dissipation by the tip in the film planes with respect to minima is given by [12, 15]

$$\Delta E_D = \frac{2}{3}\frac{r_c \alpha_{Si}}{z_0^2}\Delta A_{SiPS} \tag{4}$$

where tip-sample adhesion, expressed by A_{SiPS} (the corresponding Hamaker constant) is considered to be the varying interaction [15], which is unaffected by cantilever tilt [16]. Here z_0 is the tip-sample separation ($\simeq$ 0.2 nm in contact [12]). Using the expression $A_{SiPS} = A_{Si}^{\frac{1}{2}} A_{PS}^{\frac{1}{2}}$ [17], where A_{Si} and A_{PS} denote the Hamaker constants of Si and aPS respectively, along with Eqns (3) and (4), the value of A_{Si} [17] and some simple algebra, we determine $\Delta A_{PS}^{(i)}$, the in-plane variation in aPS Hamaker constant and hence $\Delta G_{PS-PS}^{(i)}$, the

(in-plane) variation in cohesion.

Figure 1(d) shows the observed variation (in solid circles) of $\Delta G^{(o)}_{PS-PS}$ with depth z across the gap between adjacent layers, for all the different R-values probed. Similarly, Figure 2(c) depicts $\Delta G^{(i)}_{PS-PS}$ variation (solid circles) over adjacent gyration spheres as a function of in-plane coordinate x, for different film thicknesses. In both cases the abscissae have been shifted arbitrarily for clarity. It is interesting to note that in all cases ΔG_{PS-PS}'s have a form that fits very well with the MPT potential given by [11]

$$\Delta G_{PS-PS}(\xi) = V_0 \cosh^{-2} \alpha\xi = g^2\alpha^2 \cosh^{-2} \alpha\xi \tag{5}$$

Here V_0 is the peak strength of the repulsive intermolecular potential, which has a quadratic dependence on $\alpha = \Lambda^{-1}$, Λ being the range of the potential (at $\xi = 2\Lambda$, $V = 0.07V_0$), and g^2 has the dimension of energy. The best fit curves of data with the MPT potential are shown in continuous lines in Figures 1(d) and 2(c) and values of V_0 and Λ obtained from these fits are given in Table 1. From this table it is clear that confinement has introduced an additional intermolecular potential whose magnitude, given by V_0, increases as film thickness is decreased but whose range remains more-or-less invariant. It should also be noted that, for a film with thickness $> 4R_g$ the in-plane potential is measurable but very small, consistent with the out-of-plane measurements. The situation is depicted in the cartoon in Figure 2(d).

In order to correlate this new intermolecular potential with some specific change in the molecular configuration of *aPS*, we have carried out vuv spectroscopy of polystyrene films with $R \simeq 2R_g$ and $R \simeq 9R_g$. Transmission spectra in the 4-9 eV range were collected in 10 meV steps at BEAR beamline of ELETTRA synchrotron, with nearly linearly polarized light (the estimated Stokes parameter $S_1 \simeq 0.5$), the electric field lying in the film plane [18]. The experimental chamber was maintained at $\sim 10^{-10}$ Torr and all measurements were done at ambient temperature. Our focus was on the pure electronic singlet transition $^1A_{1g} \rightarrow ^1 E_{1u}$ involving the pendant benzene rings of *aPS*, which is centered around 6 eV.

Figures 3 show this spectral band for 180.0 nm (a) and 50.0 nm (b) thick *aPS* films. The split in the band can be explained as arising from the resonant transfer interaction between correlated clusters of pendant benzene rings, given by $J_\beta = \Delta\nu/2 \simeq 428\ meV$, where $\Delta\nu$ is the measured split [19], which causes the mixing of the singly excited states of individual benzene rings through their transition dipole moments. The doublet splitting indicates

that 'dimers' of benzene rings are involved in these clusters. The intensity ratio of the high energy (-) and low energy (+) components of the doublets, $I_+/I_- = (1+\cos\alpha)/(1-\cos\alpha) = \cot^2(\alpha/2)$ gives α, the angle between the transition dipoles, i.e. the dihedral angle between rings of the 'dimer' [20], since the transition dipole is entirely in the ring-plane. The strong electronic band gives a clear indication of the change in the value of α between the two films from the change in intensities of these components. α goes from $\simeq 75°$ to $\simeq 0°$ as film thickness goes from 180.0 nm to 50.0 nm, corresponding to an 'oblique' or *ob* configuration (shown schematically in inset, Figure 3(a)) and a 'head-to-tail' or *ht* configuration (inset, Figure 3(b)) [19], respectively. A benzene 'dimer' has a permanent dipole moment only when rings are non-parallel [21], hence the *ht* 'dimer' will have near-vanishing dipole moment. This would make it undetectable through standard spectroscopic techniques [21] and to our knowledge this is the first direct experimental evidence of this 'near-parallel' benzene 'dimer'. Reduction in 'dimer' dipole moment due to this configurational change would reduce coupling between gyration spheres containing such 'dimers'. We suggest that this is manifested as the repulsive MPT intermolecular potential.

We have found a completely new phase of atactic polystyrene under confinement - the *nanoconfined phase*, more ordered than the (inherently disordered) bulk but less cohesive. Observation of similar phases in a simple fluid [3] indicates the universality of this phase and also shows a limit to which simple and complex fluids have the same behavior. We show here that in *aPS* this phase is achieved through the alignment of adjacent benzene rings, explaining the similarity of confined *aPS* to the helically ordered phases of syndiotactic *PS*, observed in infrared spectra [22]. The contradictory properties of this phase may explain its other observed properties, in particular its solid-liquid duality [7], reduction of T_g with confinement and its dependence on R_g, and return to bulk T_g-value on adding small-molecule diluents [6, 23]. This phase would also usher in new concepts in miscibility and solvation.

[1] C.-J. Yu et al, Phys. Rev. Lett. **82**, 2326 (1999); M.J. Zwanenburg et al, Phys. Rev. Lett. **85**, 5154 (2000); S.E. Donnelly et al, Science **296**, 507 (2002).

[2] M. K. Sanyal, J. K. Basu, A. Datta, and S. Banerjee, Europhys. Lett., **36**, 265 (1996).

[3] O.H. Seeck et al, Europhys. Lett. **60**, 376 (2002).

[4] M. Doi and S. F. Edwards, *The Theory of polymer dynamics*, Clarendon Press, Oxford, 1986.

[5] A.L. Demirel and S. Granick, J. Chem. Phys. **117**, 7745 (2001); M. Mukherjee et al, Phys. Rev. E **66**, 061801 (2002); J. Schuster, F. Cichos and C. v. Borzcyskowski, European Polymer Journal **40**, 993 (2004).

[6] M. Alcoutlabi and G. B. McKenna, J. Phys.: Condens. Matter **17**, R461 (2005).

[7] S. Patil, G. Matei, A. Oral and P.M. Hoffmann, Langmuir **22**, 6484 (2006).

[8] S. Chattopadhyay and A. Datta, Phys. Rev. B **72**, 155418 (2005).

[9] M. Muthukumar, Phys. Rev. Lett. **86**, 3188 (2001); C. Y. Kong and M. Muthukumar, J. Chem. Phys. **120**, 3460 (2004).

[10] A. Cacciuto and E. Luijten, Nano Letters **6**, 901 (2006).

[11] S. Flügge, *Practical Quantum Mechanics*, Springer International Student Edition, Narosa Publishing House, New Delhi, 1979.

[12] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, New York, 1992)

[13] M. G. Cacace, E. M. Landau and J. J. Ramsden, Q. Rev. Biophys. **30**, 241(1997).

[14] J. Tamayo and R. Garcia, Appl. Phys. Lett. **71**, 2394 (1997); J. Tamayo and R. Garcia, Appl. Phys. Lett. **73**, 2926 (1998).

[15] A. Schirmeisen and H. Hölscher Phys. Rev. B **72**, 45431 (2005).

[16] L.-O. Heim, M. Kappl and H.-J. Butt, Langmuir **20**, 2760 (2004).

[17] A. Sharma and J. Mittal, Phys. Rev. Lett. **89**, 186101 (2002); C. Bollinne et al, Eur. Phys. J. E **12**, 389 (2003).

[18] S. Nannarone et al, AIP Conf. Proc. **705**, 450 (2004); L. Pasquali, A. De Luisa and S. Nannarone, AIP Conf. Proc. **705**,1142 (2004).

[19] M. Pope and C. E. Swenberg, *Electronic Processes In Organic Crystals* (Oxford University Press, New York, 1982).

[20] S. Chattopadhyay and A. Datta, Chem. Phys. Lett. **391**, 216 (2004).

[21] K.C. Janda et al, J. Chem. Phys. **63**, 1419 (1975); S. Tsuzuki et al, J. Chem. Phys. **117**, 11216 (2002).

[22] V. Lupaşcu, S.J. Picken and M. Wübbenhorst, Macromolecules **39**, 5152 (2006).

[23] J. A. Forrest, K. Dalnoki-Veress, J. R. Stevens, and J. R. Dutcher, Phys. Rev. Lett. **77**, 2002 (1996); C.J. Ellison, R.L. Ruszkowski, N.J. Fredin and J.M. Torkelson, Phys. Rev. Lett. **92**, 095702 (2004).

Figure captions

FIG. 1: (color online) (a): X-ray reflectivity data (circles, Fresnel reflectivity normalized and upshifted) and fits (lines) of polystyrene (PS) films on quartz with different thicknesses R (shown beside each curve). (b): Electron Density Profiles (EDPs) along film depth from reflectivity fits, color-coded and presented in same sequence. (c): $\Delta A_{PS}^{(o)}$, increase in free energy due to layering, versus (R_g/R), R_g = unperturbed gyration radius of PS (20.4 nm). Circles: data, Line: best fit with $K(R_g/R)^b$. (d): $\Delta G_{PS-PS}^{(o)}$, variation of cohesion versus depth z, for R-values shown. Circles: data, Line: best fit with modified Pöschl-Teller (MPT) function. Curves side-shifted for clarity.

FIG. 2: (color online) Phase images of tapping-mode Atomic Force Microscopy (AFM) scans ($500nm \times 500nm$) of PS films with R = 50.0 nm ($\simeq 2R_g$)(a) and 84.0 nm ($\simeq 4R_g$)(b). (c): $\Delta G_{PS-PS}^{(i)}$, variation of cohesion versus in-plane co-ordinate x, for different R-values shown. Circles: data, Line: best fit with MPT function. Curves have been side-shifted for clarity. (d): Schematic of the confined system.

FIG. 3: (color online) Transmission spectra (absorbance versus photon energy) in vacuum ultra-violet (vuv) for PS films with R = 180.0 nm (a) and 50.0 nm (b). Assigned transitions presented beside spectral bands. Circles: data, red line: convolution of individual gaussian fits (only those for 'dimer' peaks shown in green). Inset: Configurations of benzene 'dimers' extracted from analysis of ${}^1A_{1g} \rightarrow {}^1E_{1u}$. α = dihedral angle.

TABLE I: Parameters of the intermolecular potential

Film Thickness (nm)	Peak strength (V_0)(mJ m^{-2})from		Range (Λ)(nm)from	
	XR [a]	AFM	XR	AFM
114	0	1.42	0	5.6
84	1.97	3.29	5.9	6.5
60.4	3.36	3.47	5.3	5.1
58.5	3.73	-	4.8	-
52	4.68	-	6.4	-
50	5.36	6.37	5.3	5.3
48.5	5.95	-	5.3	-

[a]X-ray Reflectivity